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Authors:

Federico Lasserre, Sebastián Suarez, Frank Mücklich

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Ultrasonic assisted polyol-reduction of H₂AuCl₄ for nanoparticle decoration of multiwall carbon nanotubes

Federico Lasserre*, Sebastian Suarez and Frank Mücklich

Functional Materials, Dept. of Materials Science and Engineering, Saarland University.

Saarbrücken D-66123, Germany

Abstract

The decoration of carbon nanotubes with metallic nanoparticles has been extensively studied for different systems. Despite the fact that several routes are available for the production of these heterostructures, their complexity and large amount of different reagents severely hinder their applicability. In this study, we propose an alternative route based on an ultrasonic assisted polyol reduction, which requires lower temperatures and amount of reagents when compared to traditional methodologies. Furthermore, the used solvent (ethylene glycol) is more environmentally friendly than other common reagents, resulting in a less aggressive process. We observed that the proposed route provides the possibility of straightforwardly tune the final nanoparticle size by controlling simple parameters such as exposure time and relative reagent concentrations. Moreover, the influence of the bath temperature has been studied, finding an upper limit of 50 °C for the proposed methodology.

1. Introduction

Recently, the combination of carbon nanotubes (CNTs) and gold nanoparticles has been explored with promising results for different applications such as: sensors [1,2], fuel cells [3], and catalysis [4,5]. However, and in order to take advantage of this hybrid structure, methods that assure a proper coating of the CNTs without considerably affecting their structure are necessary. These methods should preferably be quick and may involve as few steps as possible. Several strategies have been developed to perform the decoration [6,7]. Among these we found the attachment of previously synthesised gold nanoparticles to CNTs. These could be performed either covalently or non-covalently [7,8]. Although relative high-order decoration can be achieved, these methods present the disadvantage of requiring large steps processes

* Corresponding author: Federico Lasserre, f.lasserre@mx.uni-saarland.de Tel./Fax.: +49 (681) 302 70539/70502

and longer time. A total different approach involves the physical deposition of gold onto CNT either by thermal evaporation, e-beam deposition or solvated metal-atom dispersed method. In all the aforementioned methods [7] the need for vacuum is a disadvantage.

Between the chemical routes we found methods that generate in-situ gold nanoparticles and deposit them onto the CNT walls within the same vial. To perform this, usually strong oxidants or large ultrasound exposure times are needed to create anchoring points for the gold seeds, which might result in a decrement of the intrinsic CNTs' properties [9]. Raghuvver et al [10] used microwaves to avoid the large ultrasound damage and the use of acids, resulting in 3 to 10 nm nanoparticles decorating the nanotubes.

To synthesize the gold nanoparticles different reducing agents have been used. These include: citric acid ($C_6H_8O_7$) [11], sodium citrate ($Na_3C_6H_5O_7$) [12] and sodium borohydride ($NaBH_4$) [13]. Citric acid, sodium citrate and sodium borohydride are well known in the synthesis of gold nanoparticles, being the first two relatively mild in comparison to the latter, which allows the creation of nanoparticles as small as 2-3 nm [13]. However, the handling of $NaBH_4$ is an issue since it will react exothermically in contact with water. Another possible route to synthesize gold nanoparticles is the polyol route with ethylene glycol (EG) as the reducing agent [10].

As reported by others authors, EG is a solvent where the CNTs can be efficiently dispersed and stabilized [14,15]. Consequently, it has been used for the decoration of CNTs with different types of nanoparticles, since it allows the reduction of the metal compound and the following decoration of CNTs' walls while keeping the CNTs apart, thus avoiding agglomeration and exposing a larger surface area where the metal nanoparticles can be formed. The different type of nanoparticles synthesized onto CNTs by the polyol route includes: Pt, Pt-Ru, [15], Sn[16], etc. However, the EG route has not been further explored for the decoration of CNTs with gold nanoparticles, except for the work of Raghuvver et al [10]. The great advantages such as high scalability [17], safe manipulation of solvents, low cost of reagents, short reaction times and circumvention of the use of any surfactant or other stabilizers makes the polyol route a quite promising and interesting one for the nanoparticle decoration of CNTs for technical applications.

In our work, we used EG as both, the solvent and reducing agent and studied the possibility of activating the reaction by ultrasound, thus avoiding the thermal input to the CNTs. Furthermore, we analysed the influence of the temperature bath, time and the amount of NaOH. Finally we compare these results with the gold decoration of CNTs in a heater with magnetic stirring.

2. Materials and Methods

Ethylene glycol (C₂H₆O₂, technical grade) was used. Gold (III) chloride trihydrate (HAuCl₄·3H₂O, CAS: 16961-25-4) was purchased from Sigma Aldrich. Multiwall carbon nanotubes (MWCNTs), commercially available as Baytubes C150P (purity: >95 %, outer diameter distribution: 5-20 nm, agglomerate size: 0.1-1 mm) were used. For each experiment 1mg of MWCNT was dispersed in 20 ml EG in a homogenizer for 5 min (WiseTis HG-15, Witeg), after that 0.125 mL of the gold compound (0.01 M in water) and the corresponding amount of NaOH was added. Finally, the solution was either ultrasonicated for 10 minutes in an ultrasonic bath (Bandelin sonorex super RK 514 BH, 35 kHz -860W) or stirred in a hot plate for the same amount of time. Finally, the solution was let cool down in a beaker glass.

The samples were characterized by field emission scanning electron microscopy (FE-SEM) using a Helios NanoLabTM 600 dual beam microscope (FEI Company) working at 15 keV and 0.86 pA.

To perform the particle analysis, Fiji (an open source platform for image analysis) was used [18]. A threshold range was set to separate in a first instance the gold nanoparticles from CNT and the Si substrate. After that watershed segmentation was applied to further separate the overlapping nanoparticles. Finally, an analysis of the particles was performed showing the outlines of each particle. This image was overlay on the original image and visual check was made to validate the segmentation. In some cases manual adjustments were made and the results recalculated.

Raman spectra were acquired with an inViaTM Raman microscope (Renishaw), working with an excitation wavelength 532 nm and a 2400 l/mm grid. A 50X magnifying microscope objective was used. The power of the laser beam at the sample surface was 0.2 mW. The resulting spectra are the mean of three spectra taken from the same spot. A cosmic rays removal filter was also applied on the measurements.

Transmission electron microscopy analysis was performed in a JEOL JEM 2010 electron microscope working at 200 kV bias equipped with an EDS detector (Oxford instruments). To acquire the SAED pattern, a camera length of 30 cm has been used.

3. Results and discussion

3.1. Effect of NaOH addition

The use of NaOH in polyol reduction has been previously reported [19] as an initiator of the reaction. NaOH not only assists in the formation of carboxylate ions by multi-electron aldehyde oxidation [15], which then will help in the reduction but in the case of MWCNT decoration, NaOH might also promote site-selective nucleation of gold nanoparticles. This comes as a consequence of the hydrogen bond interaction between EG and NaOH which leads to a distribution of OH⁻ groups all over the CNT surface, that will act as anchoring points for the precipitation of gold ions [20].

The equilibrium constant (K_e) for the polyol reduction can be described by the following equation:

$$\ln K_e = nF\Delta E/RT$$

Where n is number of electrons, F is Faraday constant, ΔE is the difference between the redox potential of the two half cells reaction, R is gas constant and T temperature. For the reduction to take place ΔE should be positive. The larger the value of ΔE , the more spontaneous the reaction is and the larger the number of nuclei that are formed. ΔE can be manipulated either by the formation of complexes or by the variation of pH [21,22].

For the first set of experiments we performed the decoration in a hot plate at 50°C. This permits to study the effect of NaOH concentration independently from the effect that US can provide to the decoration. In Figure 1 we can observe how the different NaOH concentrations strongly affect the coating results.

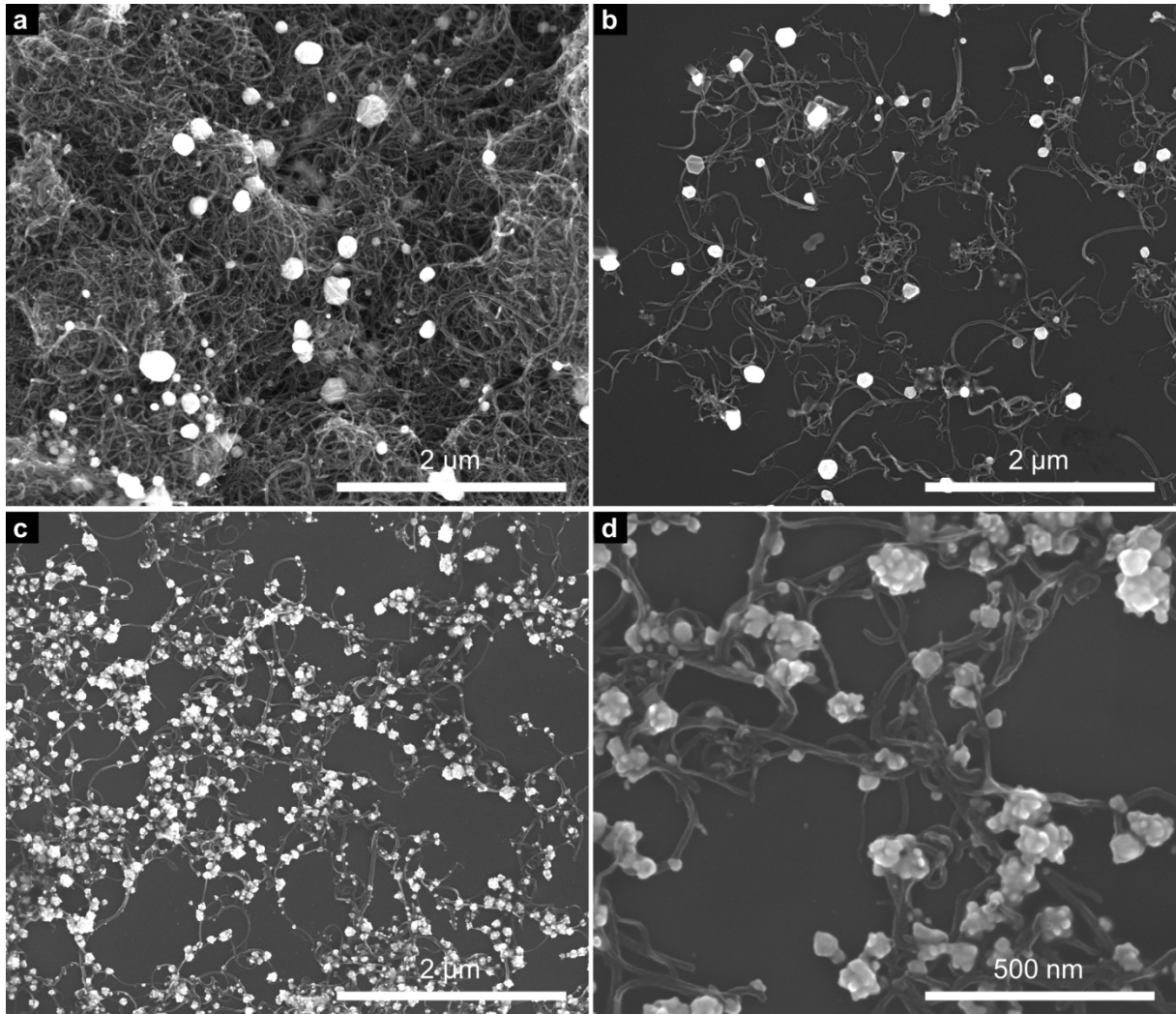


Figure 1: Influence of the amount of NaOH on the decoration of CNTs with gold nanoparticles in a heater. (a) Without the addition of NaOH, (b) 2:1 (mol NaOH : mol H AuCl₄), (c) 8:1 (mol NaOH : mol H AuCl₄) and (d) magnification of (c), respectively.

In the samples without NaOH almost no decoration was seen after 10 min in the heater at 50 °C with continuous stirring. The limited amount of particles observed presented a mean Feret diameter of around 115 ± 77 nm (Roundness: 0.86 ± 0.1) as shown in Figure 1(a). When the amount of NaOH moles doubled the amount of the gold precursor, the resulting mean Feret diameter resulted in values of 112 ± 46 nm (Roundness: 0.89 ± 0.06) as observed in Figure 1(b). The addition of NaOH neither generated more nanoparticles nor changed the obtained mean diameter. However, when the amount of the base was augmented to 8:1 (mol NaOH : mol H AuCl₄), a completely different result has been achieved. Here, the MWCNTs presented gold nanoparticles all over their surface and no uncoated MWCNT could be detected (Figure 1(c)). These results is in agreement with that reported by Chen et al. for the fabrication of Pd nanoparticles with EG as the reducing agent [23]. They detected a

proportional relation between the number of decorating nanoparticles and the amount of NaOH present. Moreover, they reported that an increment in NaOH concentration led to a reduction of the nanoparticles and more spherical morphology. In our case, the mean Feret diameter was 47 ± 32 nm and the mean roundness was 0.76 ± 0.13 . As first sight this last number does not fully agree to those of Chen but a closer look to Figure 1(c) reveals that the features decorating the CNTs' surface are composed of small spherical nanoparticles that are aggregated. Liu et al [24] described such morphology when highly alkaline conditions were used in the synthesis of magnetite nanocrystals with EG, as a consequence of an isotropic growth follow by crystallization. Zhang et al. [25] also reported that at higher pH, smaller gold nanoparticles decorated CNTs when using UV as reducing medium. Li et al. also described that working at higher pH helps in the synthesis of narrow the distribution size of the generated Pt nanoparticles which are also well distributed in the surface of the multiwall nanotubes used in their experiments [26].

The results above suggest that by varying the concentration of NaOH, the amount and size of the decorating gold nanoparticles can be tuned. However, the fact that the reaction took place in a heater with stirring produced a vortex where some CNTs tend to agglomerate.

3.2. Effect of the processing in an ultrasound bath

An important aspect to justify the use of ultrasound is that it helps in the separation of the CNTs agglomerates, keeping the CNTs isolated for a proper decoration and constitutes a regular step in the decoration with gold nanoparticles. Therefore, it would be interesting to properly explore the possibility of a simultaneous decoration and dispersion of the MWCNTs. However, the carbon nanotubes integrity might be in risk if prolonged US times are applied [27]. We have found that by combining 5 min in a homogenizer to reduce the initial agglomeration and afterwards 10 min of US helped us maintain the US time at a minimum and achieve a proper dispersion at the same time [14].

In order to see if it was possible to reduce the size of the final attached particles we performed the polyol reduction in an ultrasound bath. Ultrasound has been known to assist in the synthesis of gold nanoparticles [28] by the formation of radicals that will help in the reduction [28,29]. Moreover, it also reduces the supersaturation level which translates into larger nucleation rate and larger amount of nanoparticles [30,31]. These are less agglomerated since the shock wave generated by cavitation helps in uniformly disperse the nanoparticles in the solvent while reducing the contact of nanoparticles and its further collapse into larger particles [31]. Finally, the use of ultrasound (US) generates the breaking of the regular CNTs

wall by debonding carbon atoms, enhancing in that way the chances of a successful gold decoration [32].

Bath Temperature effect

To investigate the effect that the US has on the decoration we performed the experiments in an ultrasonic bath at different bath temperatures (Figure 2): room temperature (RT), 50 °C and 75 °C without any addition of NaOH.

In the case of the RT (Figure 2(a)) and 50 °C (Figure 2(b)) samples, only gold seeds were found decorating some CNTs. For the higher temperature sample (Figure 2(c)) the increased temperature led to the formation of a larger amount of gold nanoparticles, however not always on the CNTs surface. These nanoparticles showed a larger dispersion in their size and their shape was not always spherical as in the other samples (Figure 2)

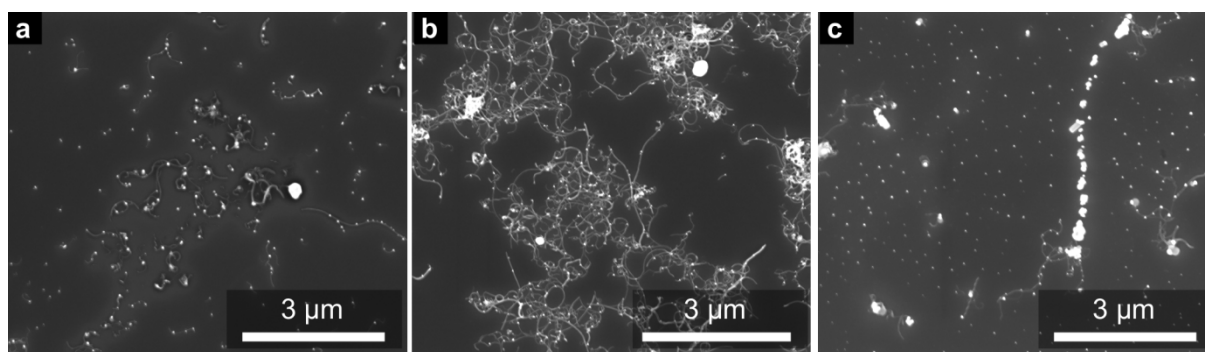


Figure 2: Bath temperature effect on the decoration of CNTs with gold nanoparticles without the addition of NaOH. (a) Room temperature, (b) 50 °C and (c) 75 °C.

Temperature has been studied in the homogeneous synthesis of different nanoparticle metals by a polyol process. Higher temperatures should lead to a diminishment in the particle size for EG reduction, but only for temperatures above 150 °C. At such temperatures the nucleation time period is fast enough to form a large number of small nuclei [33]. However, in our case, we were not interested in the homogeneous (nanoparticle free growth in the solvent) formation of nanoparticles, but on the CNTs walls (so-called heterogeneous nucleation). This is supported by the fact that only a small amount of the synthesized nanoparticles were observed in the supernatant, whereas the larger amount is attached to disperse CNTs. This behavior was detected in both, the sonication-assisted and the non-sonicated samples. Therefore, we would not recommend working above 50 °C if only decoration of MWCNT is sought. Moreover, higher ultrasonic bath temperatures leads to

higher energy consumptions and could also generate less cavitation power, since the vapour pressure is higher [34].

From the previous results we decided to further investigate the decoration of MWCNT at RT and 50 °C bath temperature with the addition of NaOH. Two molar ratios of NaOH:HAuCl₄ were studied, namely, 2:1 and 8:1.

For the 2:1 ratio no significant improvement could be seen when compared to the samples without NaOH, neither for the RT nor for the 50 °C samples. In fact, scarce deposition of nanoparticles can be found decorating the MWCNT surface. For the case of 50 °C, nanoparticles measuring in average 80 ± 6 nm can be detected. Despite being smaller than those prepared without the use of ultrasound, the amount is still negligible.

The samples prepared with higher amount of NaOH (8:1) clearly reveal an increment in the amount of decorating particles as shown in Figure 3. In both cases the mean Feret diameters were smaller than those obtained by performing the synthesis in the hot plate. The values of the mean Feret diameter for the sample prepared at RT were 11 ± 7 nm, and for the sample at 50 °C 15 ± 11 nm. The mean roundness was 0.87 ± 0.16 and 0.84 ± 0.15 for the RT and 50 °C sample, respectively (Figure 3). The nanoparticle sizes were reduced by a factor of two in the samples synthesized in the ultrasound bath. Therefore, the use of ultrasound helps to achieve a more homogeneous coating.

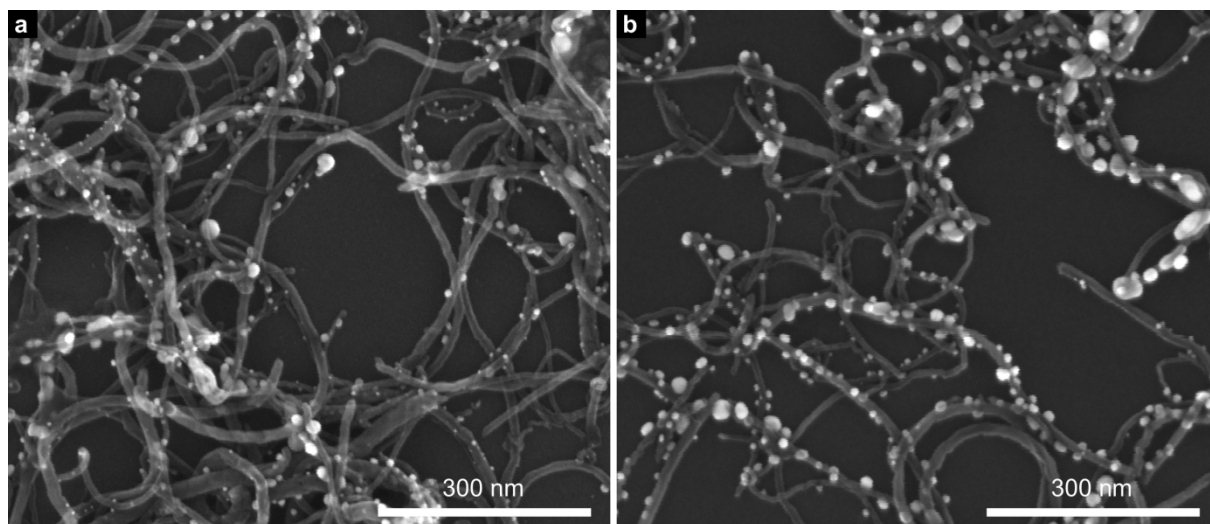


Figure 3: CNT decorated with Au nanoparticles with 8:1 (NaOH:HAuCl₄) molar ratio at different bath temperatures. (a) Room temperature and (b) 50 °C.

It may be worth noting that also for 5 min and a molar ratio of 8:1 (NaOH:HAuCl₄), decoration of CNTs is detected; though at 10 min, a better decoration and dispersion is achieved. This can be explained by the observation of the Raman spectra peaks (Figures 4 a

and b). D band (around 1350 cm^{-1}) is associated with CNTs structural defects and/or impurities. G band (around 1590 cm^{-1}) is related to the tangential vibration of the carbon atoms within the nanotube structure and its broadening / splitting (as observed in Figure 4 b) may be attributed to different modes in outer and inner shells in addition to shell-shell interactions[35]. Finally, around 2700 cm^{-1} , there is an overtone of D band (G' band) which is related to the purity of the sample [35]. Frequent Raman indicators to attest the amount of defects and purity are I_D/I_G and $I_{G'}/I_D$, respectively. Lower I_D/I_G value represents lower amount of defects, whereas higher $I_{G'}/I_D$ values denote a higher sample purity [36]. The 5 min samples I_D/I_G and $I_{G'}/I_D$ ratios were 1.09 ± 0.01 and 0.79 ± 0.05 , respectively. For the 10 min samples, 1.15 ± 0.12 and 0.72 ± 0.20 were calculated. All the measurements were performed without the addition of either NaOH or H₂AuCl₄ to evaluate the effect of ultrasound. As it was expected, larger sonication times increased the amount of defects, and therefore the number of potential chemically active sites.

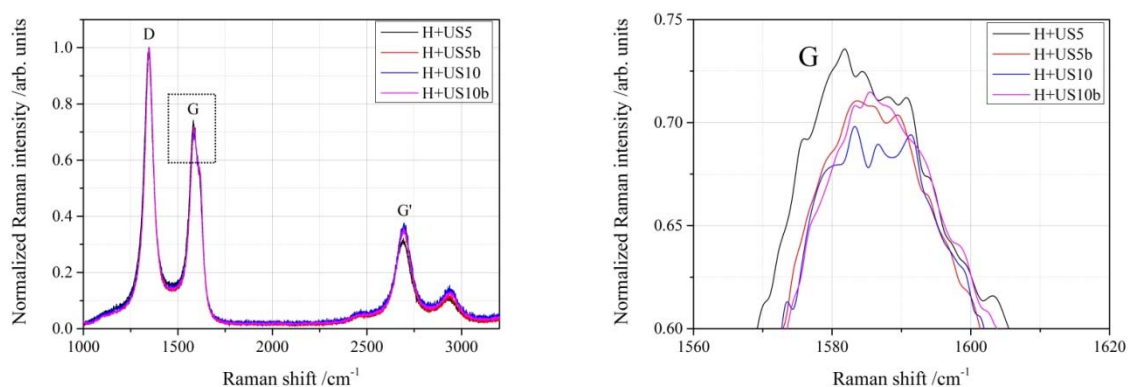


Figure 4: Raman spectra of CNTs after being submitted at 10 min homogenizer and 5 min (H+US5 and H+US5b) and 10 min (H+US10 and H+US10b) ultrasonication, respectively. D, G and G' bands associated to CNTs can be seen on the spectra. Inset in the right shows a magnification of the G peak.

Finally to characterize the nanoparticles, SAED of the samples produced at RT and with higher amount of NaOH (8:1) allows us to fully assess the decorated nanoparticles. As shown in the EDX (Figure 5 b) only gold, carbon and copper are detected, being the presence of the latter due to the support copper grid. Moreover, the SAED (Figure 5 c) matched the typical gold fcc reflections (ICDD card No.04-0784). The d-spacing of the MWCNTs (0.3479 nm correlates with that of the (002) graphite (ICDD card No.56-0159) . From these measurements we can conclude that the MWCNTs have been decorated with gold nanoparticles by a polyol-reduction of the H₂AuCl₄ added by the use of ultrasound.

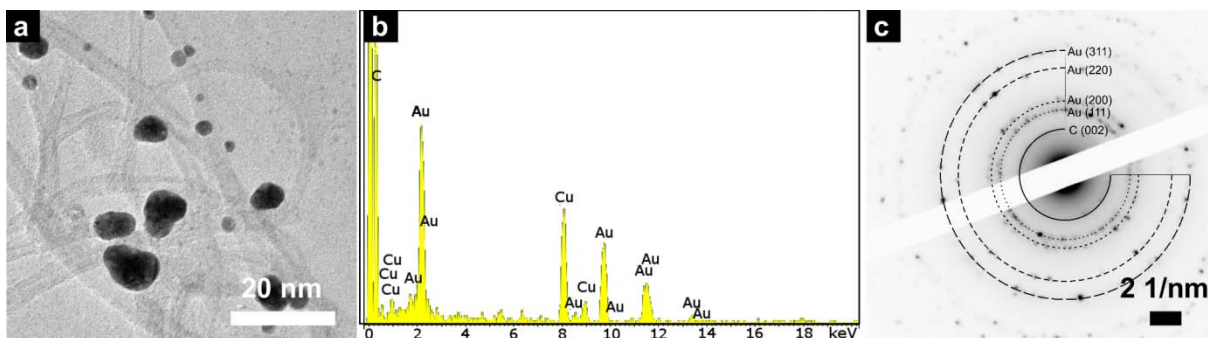


Figure 5: TEM analysis: (a) CNT decorated with Au nanoparticles with 8:1 (NaOH:H₂AuCl₄) molar ratio at room temperature (b) EDX spectra of area in image “a”. (c) SAED pattern of a gold decorated nanoparticle showing a fcc structure and the reflection associated to the MWCNTs.

4. Conclusion

We have demonstrated that it is feasible to obtain a regular decoration of MWCNTs’ surface with gold nanoparticles by an in-situ polyol reduction of a gold precursor. The main advantage of this method is the possibility of performing a coating of MWCNTs throughout a dispersion process.

The use of ultrasound not only dispersed the MWCNTs but help in the decoration of the nanotubes by creating anchoring points where the gold nanoparticles generate. By adjusting the temperature and the amount of NaOH, the homogeneity in particle size and distribution on the MWCNTs surface can be tailored. Temperatures higher than 50 °C leads to generation of nanoparticles also in the solvent, and not onto the MWCNTs surface, therefore should be avoid. In the case of NaOH, the increment of the basis leads to the generation of more homogeneous, rounded and smaller nanoparticles decorating the MWCNTs.

Summarizing, this study shows the feasibility of decoration of MWCNTs with gold nanoparticles without the need of toxic-reducing agents, low amount of chemical reagents and avoiding the use of capping agents, as opposed to what is widely reported in the literature. These results should be further developed and extended to the decoration of MWCNTs with other nanoparticles.

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